N. M. Livanova, A. A. Popov, G. E. Zaikov

STRUCTURE OF THE INTERFACIAL LAYER IN BLENDS
OF ELASTOMERS WITH DIFFERENT POLARITIES

The effects of isomers of butadiene units, the ratio of comonomers in ethylene–propylene–diene terpolymers, and the degree of isotacticity of propylene units on the intensity of interfacial interaction in covulcanizates have been analyzed.

Изучено влияние изомерных бутадиеновых звеньев, соотношения сомономеров в этилен-пропилен-диеновом сополимере и степени изотактичности пропиленовых звеньев на интенсивность межфазного взаимодействия в совулкангизатах.

Introduction

Formation of a strong interfacial layer is the key factor of the mechanism describing retardation of ozone degradation of a diene rubber by elastomer additives with a low degree of unsaturation [1-3]. The effect of comonomer ratio in ethylene–propylene–diene terpolymers (EPDMs) and stereoregularity of propylene units on the interfacial interaction and the amount of crosslinks in the interfacial layer was considered for heterophase crosslinked blends with butadiene–acrylonitrile rubbers (BNRs) of different polarities.

The density of the interfacial layer and the amount of crosslinks in it were determined via study of the swelling in the selective solvent *n*-heptane (the Zapp method [4]) through deviation of the equilibrium degree of swelling from the additive value –α (equation) [5]:

$$-\alpha = [(Q_{ad} - Q_{eq})/(Q_{ad} - Q_2)] \times 100\%,$$

where Q_{eq} is the equilibrium degree of swelling of a covulcanizate; Q_{ad} is the additive value of swelling in a given solvent, as calculated from the equilibrium degree of swelling of vulcanizates for each rubber; and Q_2 is the share of swelling of the second elastomer (BNR).

It was proposed that the interfacial layer in the crosslinked blend of copolymers with different polarities may develop via diffusion penetration of EPDM units into the nonpolar regions of BNR [6].

The objects of research in this study were heterophase crosslinked BNR–EPDM (70 : 30) blends. At this content of the nonpolar component, a system of interpenetrating crosslinked networks appears. Commercial nitrile–butadiene rubbers (trademarks BNKS-18, BNKS-28, and BNKS-40) were used. The AN-unit contents were 18, 28, and 40 wt %, respectively, and the values of the Mooney viscosity (at 100°C) were 40–50, 45–65, and 45–70 rel. units, respectively.

The content of *trans*-1,4-, 1,2-, and *cis*-1,4-units of butadiene was estimated via IR spectroscopy (bands at 967, 911, and 730 cm^{-1}) [7] with the use of extinction coefficients from [8] (Table 1).

Table 1 - Isomeric composition of butadiene units in different BNR

Copolymer	Content of units, %		
	trans-1,4-	1,2-	*cis*-1,4-
BNKS -18	82.0	8.2	9.8
BNKS -28	76.4	14.4	9.2
BNKS -40	93.0	4.4	2.6

EPDM of the Royalen brand (Uniroyal, USA), of the Keltan brand the DSM 778, 714, and 712 brands (DSM N.V., Netherlands) and the domestic EPDMs having different relative amounts of ethylene, propylene, and ethylidene norbornene (ENB) units and different degrees of microtacticities of the propylene sequences respectively, were used [7, 9, 10]. The domestic EPDMs having different relative amounts of ethylene, propylene, and ethylidene norbornene (ENB) units and different degrees of microtacticities of the propylene sequences respectively, were used [7, 9, 10]. The composition, the molecular-mass characteristics, the Mooney viscosity, the isotacticity of EPDM propylene units according to IR data are given in Table 2

Table 2 - Composition and basic characteristics of EPDMs

EPDM brand	Ethylene : propylene, wt %	Isotacti-city, %	ENB con-tent, wt %	Mooney viscosity at 125°C
R 512	68/32	20	4,0	57
R 505	57/43	24	8,0	55
R 521	52/48	22	5,0	29
778	65/35	13	4.5	63
714	50/50	12	8,0	63
712	52/48	11	4,5	63
EPDM-40	70/30	29	4,0	36-45
Elastokam 6305	74/26	9,5	5,4	67
EPDM-60(I)	60/40	13	4,0	60
EPDM-60(II)	60/40	13	6,7	62
Elastokam 7505	60/40	9,5	5,1	83

For domestic EPDMs the data on the Mooney viscosity; the content of ethylene, propylene, and ethylidenenorbornene units according to the manufacturer data.

A vulcanizing system for NBRs had the following composition, phr: stearic acid, 2.0; Sulfenamide Ts (*N*-cyclohexylbenzothiazole-2-sulfenamide), 1.5; zinc oxide, 5.0; and sulfur, 0.75. EPDM of the Royalen brand, the DSM and domestic EPDM was vulcanized with supported Peroximon F-40 taken in an amount of 5.5 phr. Each rubber was mixed with its vulcanizing system by roll milling at 40–60°C for 15 min. Then, a rubber blend was prepared under the same conditions. The blends were vulcanized at 170°C within 15 min.

Let us assume that the major fraction of polar units of BNR is uninvolved in its formation and the value of $-\alpha$ was recalculated to the 100% content of butadiene units $-\alpha^{100\%}$ (Fig. 1) and used to characterize the structure of the interfacial interaction zone and the amount of crosslinks contained in it. In such a manner, the effect of the interfacial layer volume could be minimized. As will be shown below, this situation may not be attained in all cases.
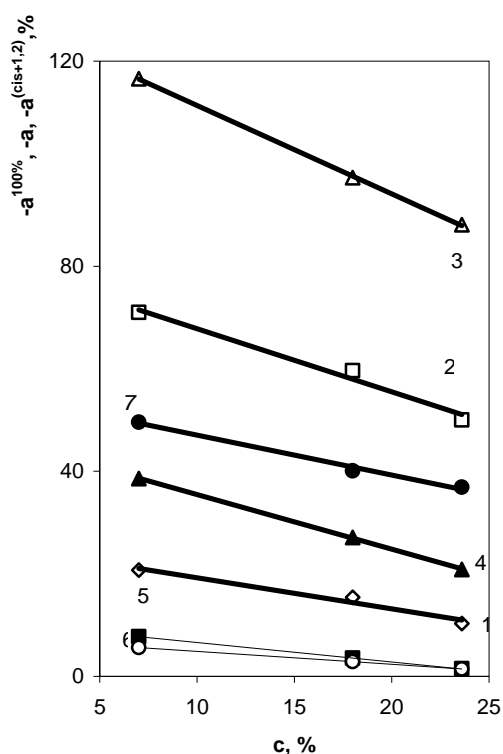

Fig. 1 - The plots the value of $-\alpha100\%$ for covulcanizates EPDM with DSM (*1*) 778, (*2*) 714, (*3*) 712, (*7*) EPDM-60(I); $-\alpha$ (*4*) for R 521; $-\alpha^{cis+1,2}$ for (*5*) R 505 and (*6*) Elastokam 6305 as a function of the total content of 1,4-*cis*- and 1,2-butadiene isomers in BNR

It is seen that a linear decrease in the value of $-\alpha^{100\%}$ with an increase in the total content of 1,4-*cis* and 1,2 units is observed for the crosslinked blends of BNR with all DSM EPDM samples and EPDM-60(I) characterized by a low isotacticity of propylene (Table 2). The fact that the value of $-\alpha^{100\%}$ decreases in

proportion to the amount of 1,4-*cis* and 1,2 isomers of butadiene units for EPDM-based blends provides evidence that the density of the transition layer increases. This circumstance implies that the mutual solubility of EPDM comonomers and butadiene units that occur for the most part in the 1,4-*trans* configuration in the neighborhood of these isomers is improved.

For DSM and EPDM-60(I) the region of interfacial interaction is bounded by nonpolar BNR units. The compatibility of chain portions of these EPDM samples with the polar acrylonitrile groups is ruled out. As the proportion of propylene units in EPDM is increased, the compatibility of the components, the density of the interfacial layer, and the amount of crosslinks in it drop sharply (the absolute value of $-\alpha^{100\%}$ increases). Thus, the higher the content of atactic propylene units in EPDM has the lower the adhesion interaction of the components and the worse its compatibility with BNR. Ordered structures worsen compatibility of polymers even to a higher extent [11].

For BNR covulcanizates with EPDM R 512 and EPDM-40 containing a large proportion of ethylene units and distinguished by the presence of stereoregular propylene sequences and small amount ENB, the value of $-\alpha^{100\%}$ linearly decreases with the content of butadiene units by a factor of 2.6 (Fig. 2) [1-3].
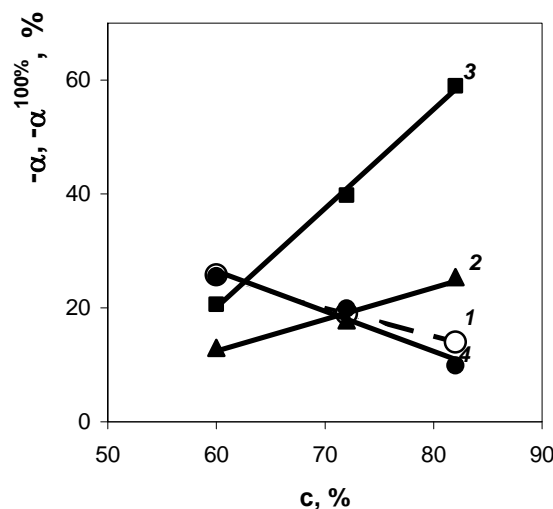
Fig. 2 - (*1,4*) ($-\alpha$) and (*2, 3*) ($-\alpha100\%$) vs. overall content of butadiene units *c* for (*1*) EPDM-40, (*2*) EPDM-60 (II), (*3*) Elastokam 7505, (*4*) EPDM R 512 in their covulcanizates with BNR

This fact leads us to infer that, firstly, ethylene units adjoining predominantly short isotactic propylene sequences are well compatible with all isomers of butadiene units. Secondly, an increase in the density of the interfacial layer and in the amount of crosslinks in it (a decrease in $-\alpha^{100\%}$) with a rise in the proportion of nonpolar units in BNR implies that EPDM molecular fragments may penetrate into BNR regions that apparently contain single polar acrylonitrile groups. EPDM-40 with a higher degree of isotacticity of propylene units (as compared with EPDM R 512) is characterized by a far more intensive penetration of

150

propylene chain fragments in their rigid isotactic configuration into BNR regions containing single polar groups (its local density reduction).

For the covulcanizates of R 521 EDPM, which contains a large amount of isotactic propylene sequences [1], the proportional decrease is observed in the $-\alpha-\Sigma$(1,4-*cis* and 1,2 units) coordinates (Fig. 1). Consequently, at a high content of isotactic propylene units, EPDM shows better compatibility with BNR. This observation may be attributed to the rigidity of isotactic propylene sequences arising from hindered conformational transitions. The potential barrier to transitions between rotational isomers of monomer units for the isotactic PP is 21 kJ/mol, while for PE, the potential barriers of *T*–*G* and *G*–*G* transitions are 2.5 and 8.8−10 kJ/mol, respectively [12].

For blends with EPDM R 505 and Elastokam 6305 with a high content of ethylene units (74%), with a higher amount of ENB (5,4%) and a very low degree of isotacticity of propylene sequences (9.5%), which contains a large amount of ENB, the linear dependence is attained when the values of $-\alpha^{100\%}$ are recalculated to the 1% of the sum of 1,4-*cis* and 1,2 units in BNR ($-\alpha^{cis\,+\,1,2}$) (Fig. 1) [1, 3]. The data presented above suggest that the chain fragments of this EPDM are well compatible only with those portions of butadiene chains that contain 1,4-*cis* and 1,2 isomers, while in the case of 1,4-*trans* units, compatibility is much worse.

EPDM-60 (II) with a higher content of ENB (6.7%) and Elastokam 7505 with degree of isotacticity of propylene units is lower (9.5%) and the Mooney viscosity is very high is compatibilized only with butadiene units ($-\alpha^{100\%}$) increases by as their content grows (Fig. 2). The higher the volume of this layer (the lower the polarity of BNR, the higher ($-\alpha^{100\%}$) values) Elastokam 7505 is characterized by the minimum compatibility with all BNR samples.

Thus, the structure of interfacial interaction zone depends on the comonomer composition of EPDM, the stereoregularity of propylene units, and the isomerism of butadiene units. The compatibility of propylene fragments of EPDM chains that predominantly occur in the atactic configuration with butadiene units is much worse in compared with EPDM with high isotacticity of propylene units. The largest amount of crosslinks in the interfacial layer forms when EPDM with a high content of ethylene units is used despite the moderate amount of diene contained in it.

References

1. Livanova N. M., *Polymer Science, Ser.* A **48**, 821-826 (2006) [*Vysokomol. Soedin., Ser.* A **48**, 1424-1430 (2006)].
2. Livanova N. M., Lyakin Yu. I., Popov A. A., Shershnev V. A., *Polymer Science, Ser.* A **49**, 63-70 (2007) [*Vysokomol. Soedin., Ser*. A **49**, 79-87 (2007)].
3. Livanova N. M., Lyakin Yu. I., Popov A. A., Shershnev V. A., *Polymer Science, Ser.* A **49**, 300-306 (2007) [*Vysokomol. Soedin., Ser*. A **49**, 465-472 (2007)].
4. *Multicomponent Polymer Systems*, Ed. by R. F. Gould (American Chemical Society, Washington, 1972.
5. Lednev Yu. N., Zakharov N. D., Zakharkin O. A., et al., *Kolloidn. Zh*. **39**, 170-173 (1977).
6. Kuleznev V. N., *Vysokomol. Soedin., Ser*. B **35**, 1391-1402 (1993) [*Polymer Science*, Ser. B **35**, 839-850 (1993)].
7. Dechant J., Danz R., Kimmer W. and Schmolke R., *Ultrarotspektroskopische Untersuchungen an Polymeren* (Akademie, Berlin, 1972; Khimiya, Moscow, 1976), p.p. 347-362, 190-233.
8. Kozlova N. V., Sukhov F. F., and Bazov V. P., *Zavod. Lab*. **31**, 968-970 (1965).
9. Kissin Yu. V., Tsvetkova V. I., and Chirkov N. M., *Doklady AN SSSR,* **152,** p.p. 1162-1165 (1963).
10. Kissin Yu. V., Popov I. T., Lisitsin D. M., et al., *Proizvod. Shin Rezino-Tekh. Asbesto-Tekh. Izdelii,* No. 7, 22-27 (1966).
11. Livanova N. M., Karpova S. G., and Popov A. A., *Polymer Science, Ser.* A **53**, 1128-1134 (2011) [*Vysokomol. Soedin., Ser.* A **53**, 2043-2049 (2011].
12. Vol'kenshtein M. V., *Configurational Statistics of Polymer Chains* (Akad. Nauk SSSR, Moscow, 1959) [in Russian].

© **N. M. Livanova** - PhD, Emanuel Institute of Biochemical Physics, Russian Academy of Sciences*;* **A. A. Popov** – DSci, professor Emanuel Institute of Biochemical Physics, Russian Academy of Sciences; **G. E. Zaikov** – DSCi, professor, Kazan National Research Tecnological university, gezaikov@yahoo.com.